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MOLLIER DIAGRAM FOR NITROGEN

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Aerodynamics Research Report No. 285

MOLLIER DIAGRAM FOR NITROGEN

by

Richard L. Humphrey and Carolyn H. Piper

ABSTRACT: Thermodynamic data for nitrogen are presented in Mollier diagram form covering the temperature range of 30°K to 15,000°K and the density range of 10^{-7} to 10^{3} amagat. Data for the solid and liquid regions are included. The diagram contains all available data of interest to the worker in fluid mechanics and aerodynamics. Speed of sound data are presented on separate charts.

U. S. NAVAL ORDNANCE LABORATORY
White Oak, Silver Spring, Maryland

Mollier Diagram for Nitrogen

This report brings together in one large scale diagram most of the available data for nitrogen. The temperature range covered is 30°K to 15,000°K while densities from 10^{-7} to 10^{3} are represented. This diagram is especially recommended for aerodynamicists and those engaged in aerodynamic facility design.

The authors acknowledge the assistance of Mr. John R. Bott who did the lettering of the diagram sheets.

E. F. SCHREITER
Captain, USN
Commander

E. L. Harris

E. L. HARRIS
By direction

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INTRODUCTION

The demand for high Mach number low altitude flight simulation in wind tunnels has increased in recent years. Wind tunnel supply temperatures and pressures have increased tremendously. Tunnels now being planned require pressures to 5000 atmospheres and temperatures to 2800°K. At conditions such as these there are wide deviations from the ideal gas and such things as variable specific heat and intermolecular forces must be considered.

The need for adequate thermodynamic property data under these conditions is evident. The past ten years have seen an outpouring of works on the thermodynamic properties of air and these properties may now be considered to be well documented. However, the study of the properties of nitrogen has only recently resulted in adequate tables for high temperatures.

Thermodynamic diagrams have several advantages over tabulated tables. One of the principal advantages is convenience. The diagram allows trends to be seen at a glance and presents masses of data in a few sheets. The required information on most common thermodynamic processes can be obtained from the diagram without tedious interpolation in tables. In most cases the accuracy of the diagram is sufficient for engineering use.

The making of thermodynamic diagrams for gases has been a popular activity among thermodynamicists and chemists for the past 60 to 70 years. Din (ref. (1)) in his three volume work on gases for industrial use gives an excellent historical and critical review of such diagrams in general (ref. (1a)) and for particular gases as he discusses them individually. Generally, industrial and chemical users have preferred the temperature-entropy diagram, for example references (1) and (2), while aerodynamicists and power plant engineers used the Mollier or enthalpy-entropy diagram (refs. (3)-(7)). The many isenthalpic and isentropic processes encountered in fluid dynamics make the Mollier diagram popular in this field.

Most of the existing diagrams for nitrogen are limited in their coverage. Almost all do not include the high density-high temperature region that is now of growing interest. A recent report by Grabau and Brahinsky (ref. (8)) gives calculated properties of nitrogen for densities to 1000 amagat. This filled in a region for which no adequate data had been available.

The large amount of recent data that is now available and the limited scope of other diagrams made it advisable to compile a new diagram which would include as much of the available data as possible. It also afforded the opportunity to compare and study the various sources of thermodynamic properties. The new diagram is presented in this report. It covers a range from 30°K to 15,000°K and a density range from log ρ/ρ_s = -7.0 to 3.0; data for the solid, liquid, and vapor regions have been included.

The sources, the compilation, and the use of the diagram will be discussed. Appendices containing information helpful in the use of the diagram have been included.

SOURCES FOR THE DIAGRAM

A great many sources were used in the preparation of the diagram. Usually each source covered only a limited region. In some cases units and reference points had to be converted. Figure 1 gives a skeleton chart showing the scope of the diagram and reference numbers for each region. In some areas the regions overlap and several sources were used.

The bulk of the data from 100 to 1500°K and a density range from log ρ/ρ_s = -7.0 to 2.8 was taken from Little and Neel (ref. (9)). Their tables incorporate the work of Din (ref. (1c)) and Hilsenrath, et al (ref. (10)) for pressures down to 10^{-2} atmospheres. They used a perfect gas extrapolation for pressures below 10^{-2} atmospheres. At the high densities, the tabulated pressures range from 10^4 atmospheres at 300°K to 10^2 atmospheres at 1500°K.

The tables of Din are based on the best available experimental data. Din believes that his worst points are no more than 1.5 percent in error while most of the tables are good to within 0.5 percent. Din made an extensive comparison of the work of many experimenters and from these chose the best data for calculating his tables.

Below 100°K the ideal gas thermodynamic functions for molecular nitrogen of Hilsenrath, et al (ref. (1)) were used to determine enthalpy levels at zero pressure and entropy values at atmospheric pressure. Temperature lines were found by assuming that $(\partial H/\partial p)_T = 0$. The values of entropy at low pressures were found from the modified perfect gas relationship.

$$(S/R)_T = (S/R)_{T,\ p = 1\ atm} - \ln p$$

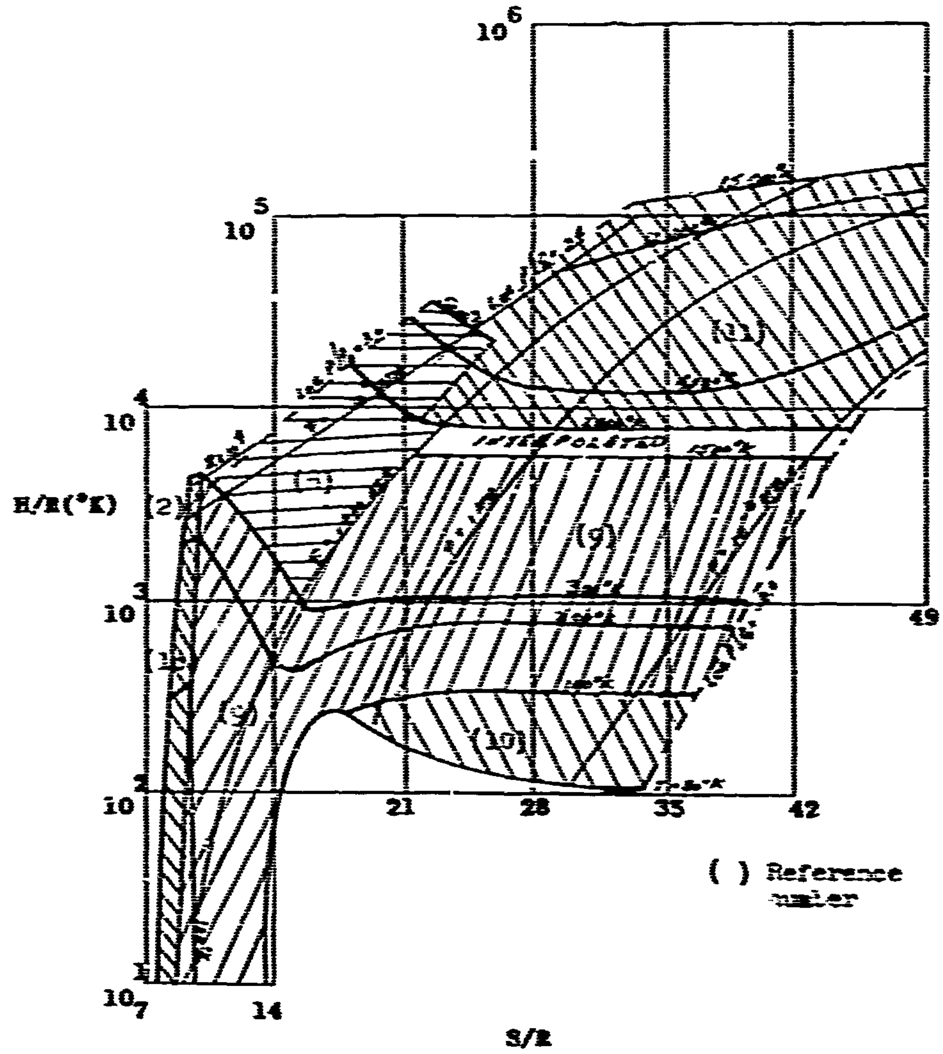

Figure 1 Skeleton Diagram Showing Sources of Data

The line connecting the critical point and the triple point was taken from Din (ref. (1c)). Some pressure and density lines near this region were taken from reference (2). This region defines the bounds between the saturated vapor and the saturated liquid. It is equivalent to the zero moisture line on a steam Mollier diagram. From the triple point to lower pressures the line of equilibrium between the solid and vapor phases (zero vapor line) was defined by the expression from Din (ref. (1c)) converted from mm Hg to atmospheres:

$$\log p = 3.61513 - \frac{(255.821)}{(T - 6.600)}$$

where T is in °K.

A discrepancy exists between the ideal gas data of reference (10) and the experimental triple point obtained from Din (ref. (1c)). The difficulty has not been resolved and caution should be used in interpreting the diagram near the zero vapor boundary below 100°K. Away from the boundary the ideal gas data should be adequate.

Data for the melting solid and the freezing liquid were taken from Din (ref. (1c)) and from reference (2). Extrapolations were made to extend these data to 1000 amagat ($\log \rho/\rho_o = 3.0$). Properties at pressures above the critical point were taken from Din (ref. (2)) and from Little and Neel (ref. (9)). The trend of the data in this region indicates that a point is reached about 1000 amagat where the solid and the liquid regions coincide.

Properties for the high temperature low density region were taken from the tables of Hilsenrath and Klein (ref. (11)). These tables include the effects of dissociation, ionization, and intermolecular forces. Intermolecular forces are included to the second virial correction. Hilsenrath and Klein use the well-known procedure of listing all of the important chemical reactions taking place, determining the amount of reactants present at each condition and calculating the thermodynamic properties of the mixture. These properties are then corrected for the intermolecular forces. The tables have been widely used and are accepted as reliable.

Grabau and Brahinsky (ref. (8)) recently compiled a set of tables for high density nitrogen (to 1000 amagat) which includes third virial corrections. These tables extend to 5000°K and have been designed to blend well with the tables of Little and Neel (ref. (9)) at low temperatures. At the higher temperatures the property values of Hilsenrath and Klein (ref. (11)), and Smith (ref. (12)) at $\log \rho/\rho_o = 0$ were used as points of departure. While Graban makes no claims for accuracy, he feels that the tables are internally consistent and are adequate for engineering use.

COMPILING THE NITROGEN MOLLIER DIAGRAM

The convenient format of Little (ref. (3)) and Humphrey, Little, and Seeley (ref. (4)) was chosen for the diagram. The dimensionless forms, such as H/RT (enthalpy), S/R (entropy), log ρ/ρ_e (density in amagat units), and P (atmospheres) used in the National Bureau of Standards (NBS) tables (refs. (10) and (11)) and those based on the NBS work (refs. (3), (4), (6), (8), and (9)) were used whenever possible. The enthalpy function is shown as H/R in units of °K. Conversion factors for various dimension systems are given in Appendix B. A table of densities corresponding to the values of log ρ/ρ_e is given in Appendix C.

Sections of the diagram are plotted on semilog paper. Each sheet covers one order of magnitude of enthalpy and seven units of entropy. An index to the sections is given in figure 2. This will aid in locating the desired sections. The diagram is cut off at a value of S/R = 49. The area of serious interest to workers in fluid dynamics lies in the region where values of entropy are low. A look at figure 2 shows that the diagram is beginning to taper to a long point bounded by T = 15,000°K and log ρ/ρ_e = -7.0. Thus only a small amount of useful information is lost by stopping the diagram at S/R = 49.

Whenever the work of Din (refs. (1c) and (2)) was used directly, the tabulated values were changed to the dimensionless values of NBS. The different reference points for zero entropy and enthalpy were also adjusted. The equations used are given in Appendix D.

The interpolation necessary to fill the low density region between 1500 and 2000°K was done graphically. Slight differences between tables were smoothed by fairing a curve through several points on the curve.

USING THE MOLLIER DIAGRAM

This section is designed to help the user of the diagram and may be considered as independent of the remainder of the text.

The Mollier diagram contains values for the pressure, density, temperature, enthalpy, and entropy of nitrogen. Temperature (°K) is represented by heavy solid lines and pressure (in atmospheres) by thin solid lines. The density (log ρ/ρ_e, ρ in amagat units) is a dashed line. Enthalpy is in units of °K and the entropy is dimensionless. Pressure, temperature, and density lines are spaced at close enough intervals that linear interpolation is adequate in most cases. The symbols used are given in Appendix A and conversion factors to obtain other units in various dimension systems are in Appendix B.

The compressibility factor, Z, may be found from the expression, $Z = P/\rho RT$. This is especially easy as R is $3.661 \times 10^{-3}(1/(273.16^\circ K))$ when P is in atmospheres, ρ in amagats, and T in °K. If T is in °R, R is $2.175 \times 10^{-3}(1/(459.69^\circ R))$. These values of R are independent of the type of gas so long as atmosphere and amagat units are used.

The index sheet, figure 2, will help to locate the proper sheets within the diagram. The sheets are numbered in columns so that an isentropic process may be followed more easily.

SOURCES FOR THE ACOUSTIC VELOCITY CHARTS

The speed of sound data were taken from Lewis and Neel (refs. (13) and (14)). They calculated specific heats and acoustic velocities from the tables of Little and Neel (ref. (9)), Hilsenrath and Klein (ref. (11)), and Smith (ref. (12)). The tables were plotted at constant density as a function of temperature to check the matching of the various sources. The acoustic velocity blended smoothly from source to source except at the very high densities. At densities of $\log \rho/\rho_0 = 2.4$ and 2.6 discontinuities exist between acoustic velocities calculated from Little and Neel and those calculated from Smith. The discontinuities are modest at $\log \rho/\rho_0 = 2.4$ but are very large at $\log \rho/\rho_0 = 2.6$. The charts probably should not be used for densities greater than $\log \rho/\rho_0 = 2.4$. The acoustic velocities are given in terms of a/a_0 where a_0 is the acoustic velocity at standard conditions. Values of a_0 are given in Appendix B. The curves are given at constant temperature as a function of $\log \rho/\rho_0$. The three charts cover the low temperature ($T < 2000^\circ K$)-low density region ($\log \rho/\rho_0 < 0$), the high temperature region ($T > 2000^\circ K$), and the low temperature ($T < 2000^\circ K$)-high density region ($\log \rho/\rho_0 > -1.0$).

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APPENDIX A

SYMBOLS LIST

a	acoustic velocity
a_*	acoustic velocity, S.T.P.
°C	temperature in degrees Centrigrade
c.p.	critical point
°F	temperature in degrees Fahrenheit
H	enthalpy
°K	temperature in degrees Kelvin
P	pressure (atm)
p_*	reference pressure
R	gas constant
°R	temperature in degrees Rankine
S	entropy
T	temperature
t.p.	triple point
Z	compressibility factor
ρ	density
ρ_*	reference density

APPENDIX B

STANDARD PROPERTIES AND CONVERSION FACTORS

1. Standard Properties

molecular weight		28.016
density of the gas at S.T.P. (international atm. g = 980.665)		0.0012525 grams/cm^3
molecular volume at N.T.P.		22,403.5 cm^3
boiling point of liquid at 1 atm.		77.35°K
triple point:	temperature	63.15°K
	pressure	94.01 mm Hg
critical constants:	temperature	126.2°K
	pressure	33.5 atm.
	volume	90.094 cm^3/mole
	density	248.668 amagat

2. Convernsion Factors

Standard Atmospheric Pressure

$P_{\bullet}$ = 760 mm Hg
29.921 in Hg
10332 kg/m^2
14.696 psia
2116 psfa

Reference Density

$\rho_{\bullet}$ = 1.25046×10^{-3} gram/cm^3
4.46338×10^{-5} moles/cm^3
1.25050 gram/liter
4.51760×10^{-5} lb/in^3
7.80461×10^{-2} lb/ft^3
2.42435×10^{-3} slugs/ft^3

Temperature

T (°K) x 1.8 = T (°R)
T (°K) = T (°C) + 273.16
T (°R) = T (°F) + 459.69

Acoustic Velocity

$a_{\bullet}$ = 1105.66 ft/sec
= 0.337006 mm/μsec
= 0.337006 km/sec

To Change	To	With Units of	Multiply By
H/R (°K)	H/RT	none	1/T (°K)
	H/R	°R	1.8
	H	ft^2/sec^2	3196.66
		BTU/lb	0.12768
		cal/gm	0.0709305
S/R	S	ft^2/sec^2-°K	3196.66
		ft^2/sec^2-°R	1775.92
		BTU/lb-°R	0.07093
		BTU/lb-°K	0.12678
		cal/gm-°K	0.0709305
ρ/ρ_o	ρ	gm/cm^3	1.25046×10^{-3}
		lb/in^3	4.51760×10^{-5}
		lb/ft^3	7.80641×10^{-2}

APPENDIX C

DENSITIES CORRESPONDING TO THE DIAGRAMMED ARGUMENTS

Log ρ/ρ_o	ρ/ρ_o (amagats)
3.0	1000.000
2.9	794.333
2.8	630.957
2.6	398.107
2.4	251.189
2.2	158.489
2.0	100.000
1.8	63.0957
1.6	39.8107
1.4	25.1189
1.2	15.8489
1.0	10.0000
0.8	6.30597
0.6	3.98107
0.4	2.51189
0.2	1.584489
0.0	1.000000
-0.2	0.630957
-0.4	0.398107
-0.6	0.251189
-0.8	0.158489
-1.0	0.100000
-1.2	0.0630957
-1.4	0.0398107
-1.6	0.0251189
-2.0	0.0100000
etc.	etc.

APPENDIX D

CONVERSION FACTORS FOR F. DIN (REF. (1c))

Din's units are:

- Entropy - joules/(mole-°K)
- Volume - cubic centimeters/mole
- Enthalpy - joules/mole

ρ/ρ_o = 2.24035 x 10^4/(tabulated value)

S/R = 1.2173 x 10^{-1} x tabulated value

H/R = (1.2173 x 10^{-1} x tabulated value) - 848.0

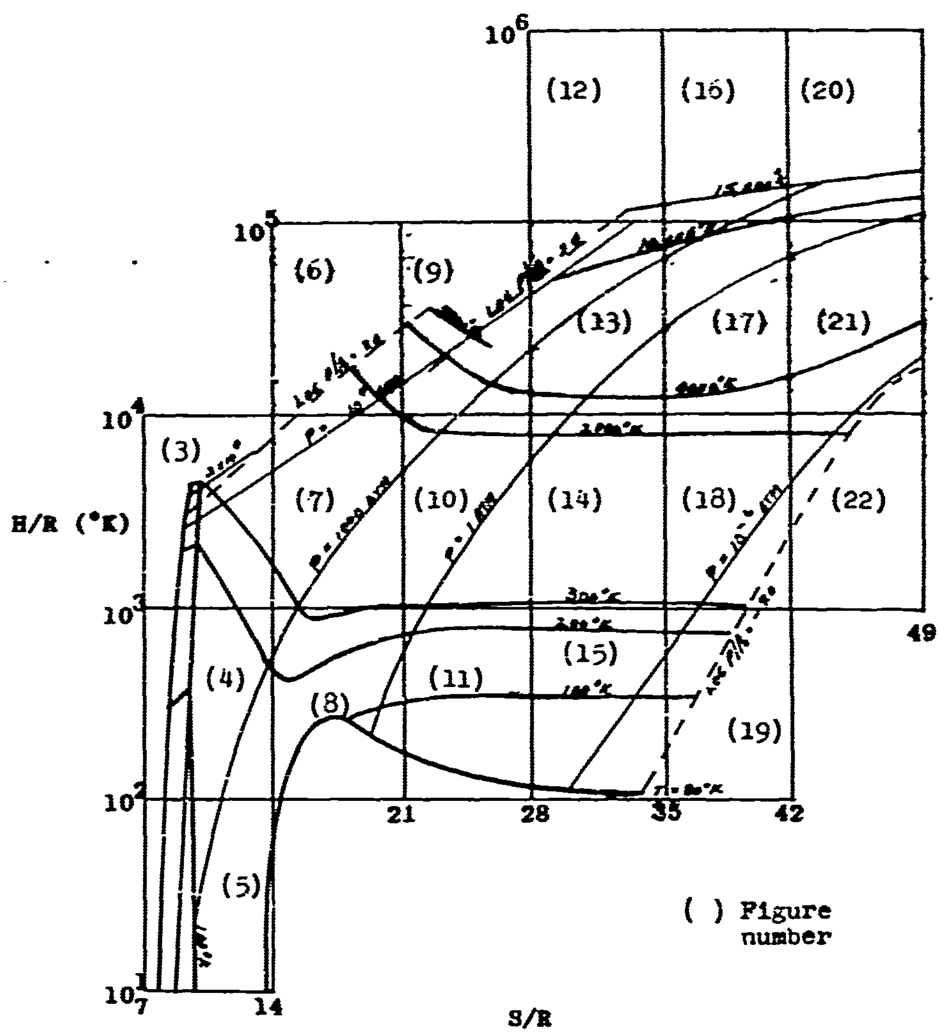


Figure 2 Index to the Nitrogen Mollier Diagram

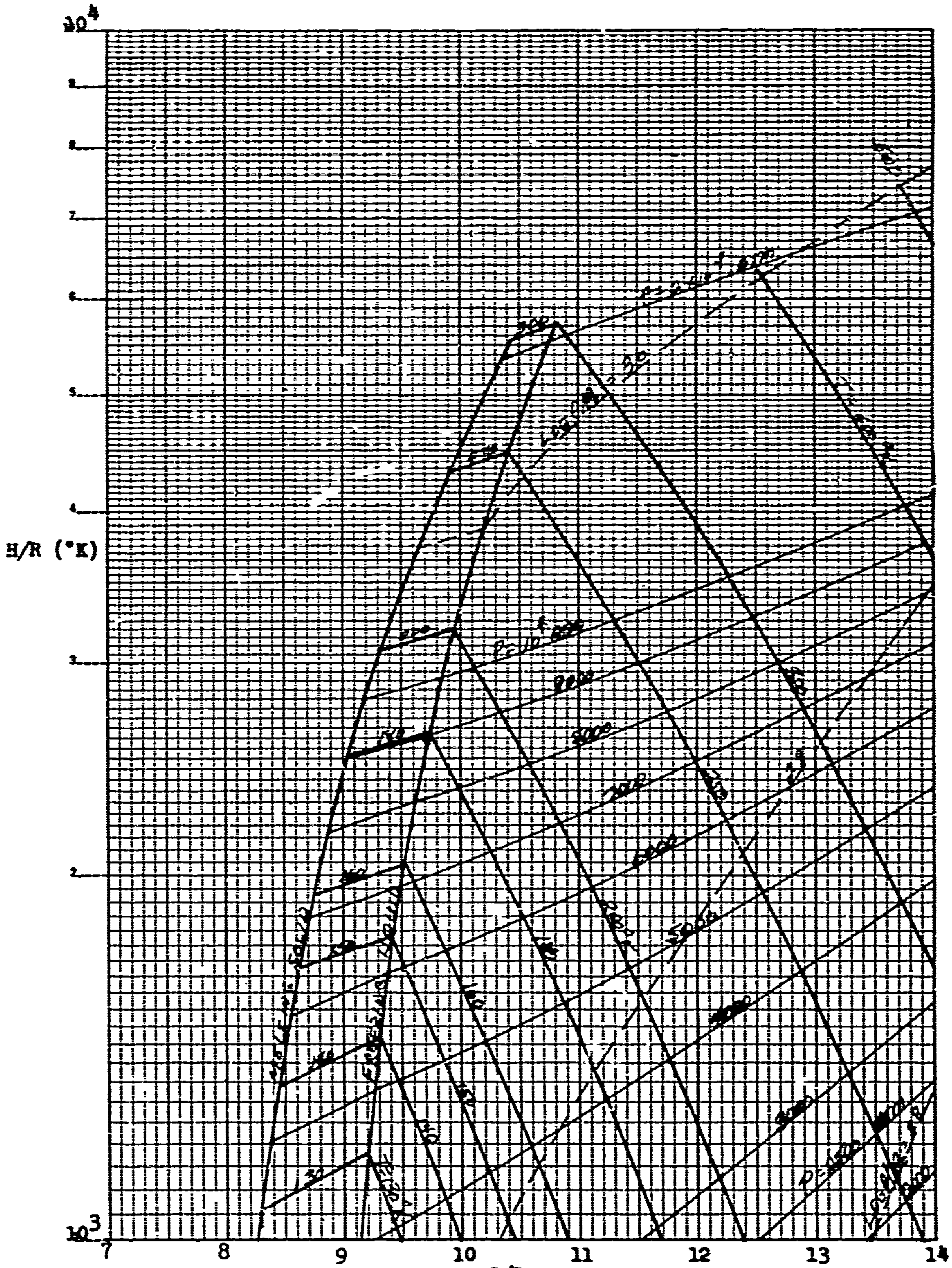


FIG. 3

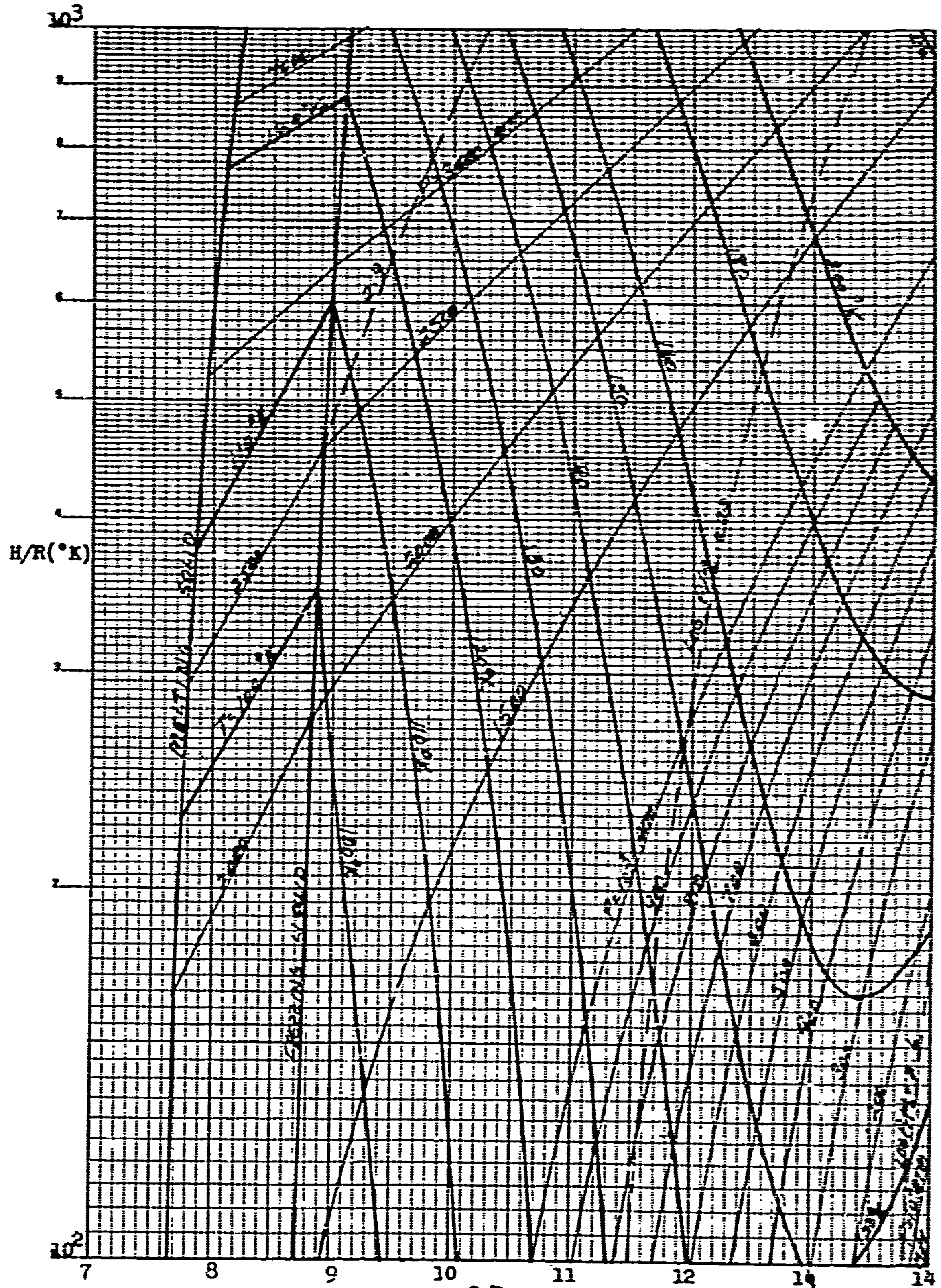


FIG. 4

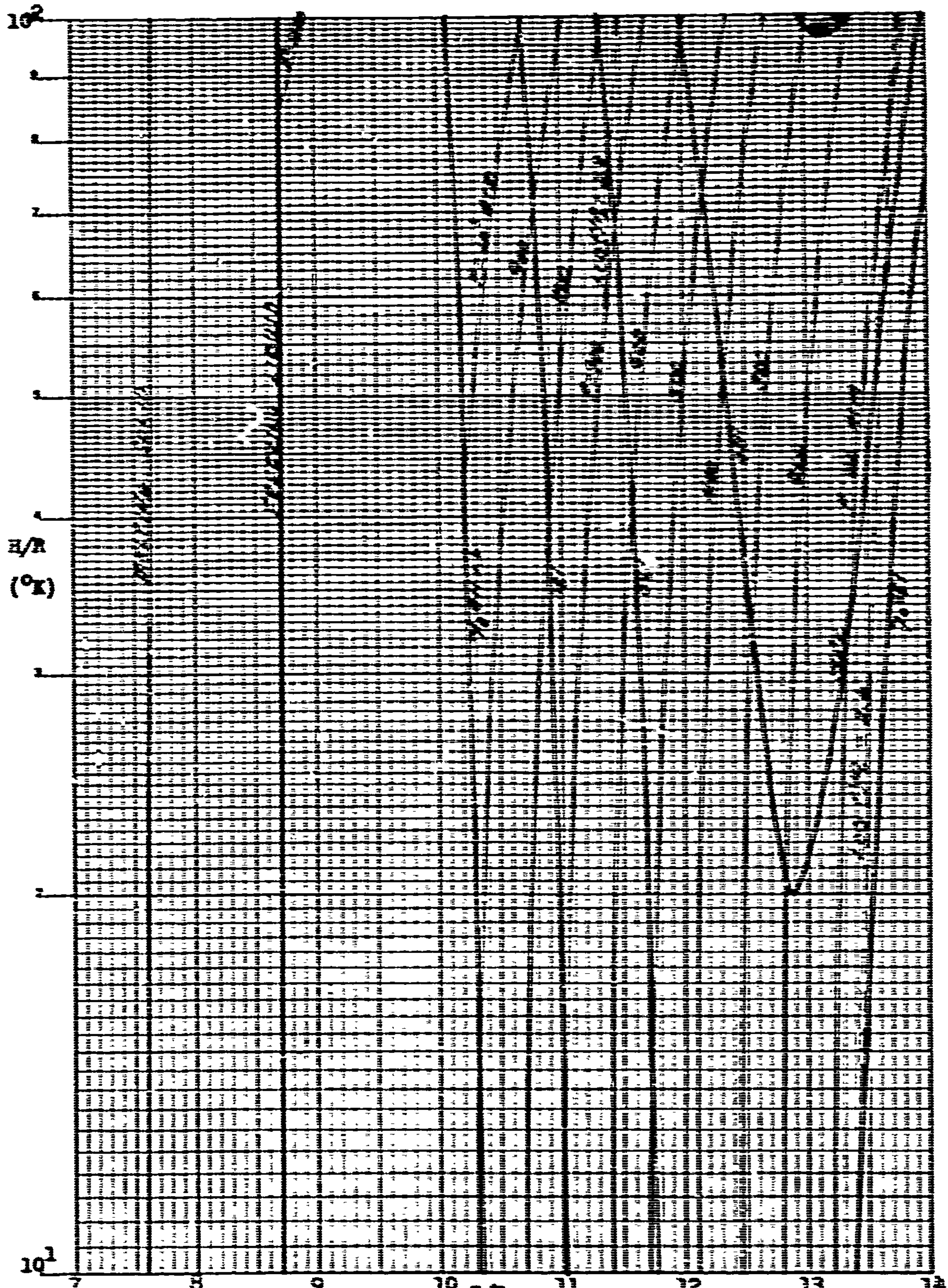


FIG. 5

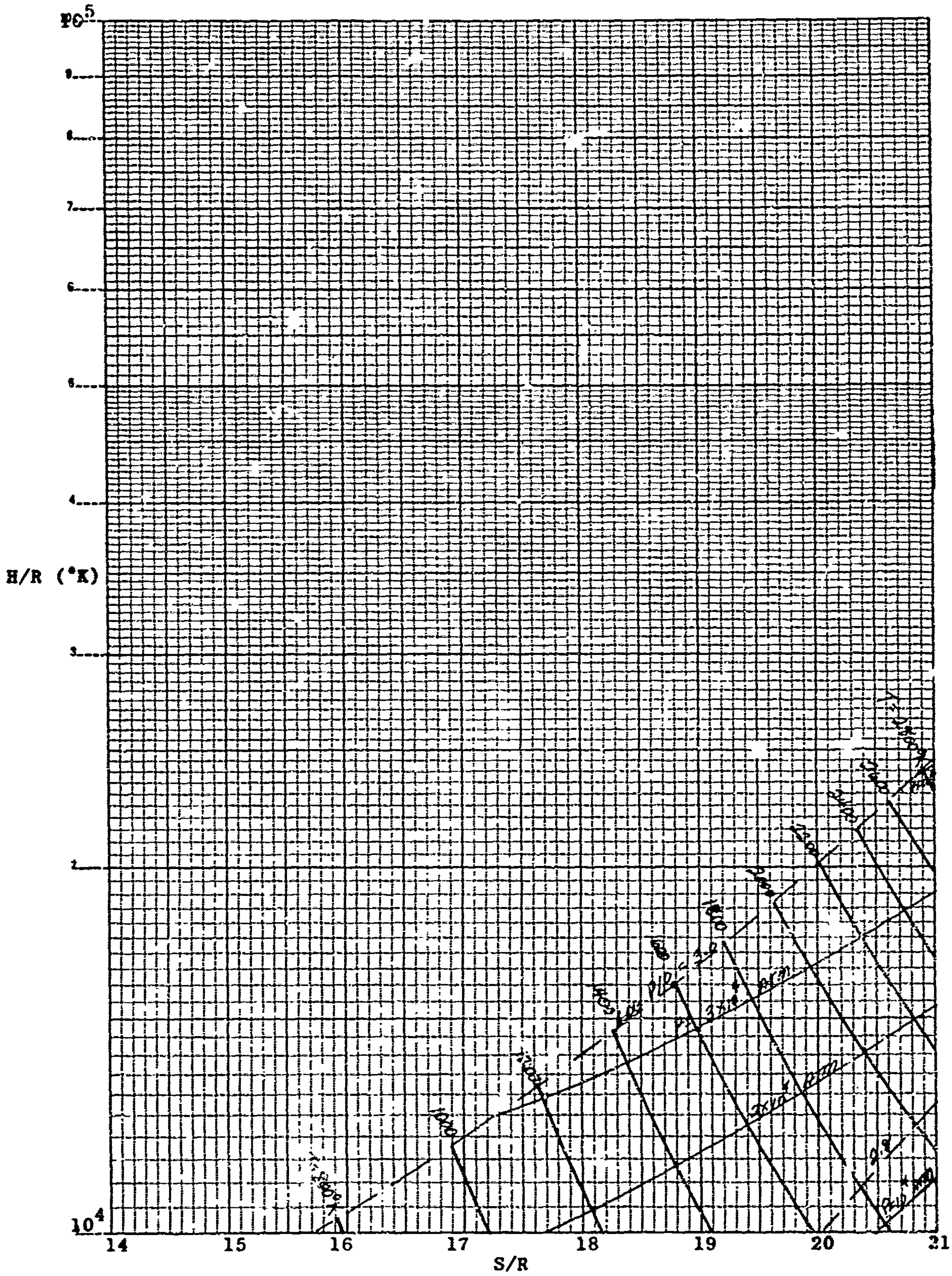


FIG. 6

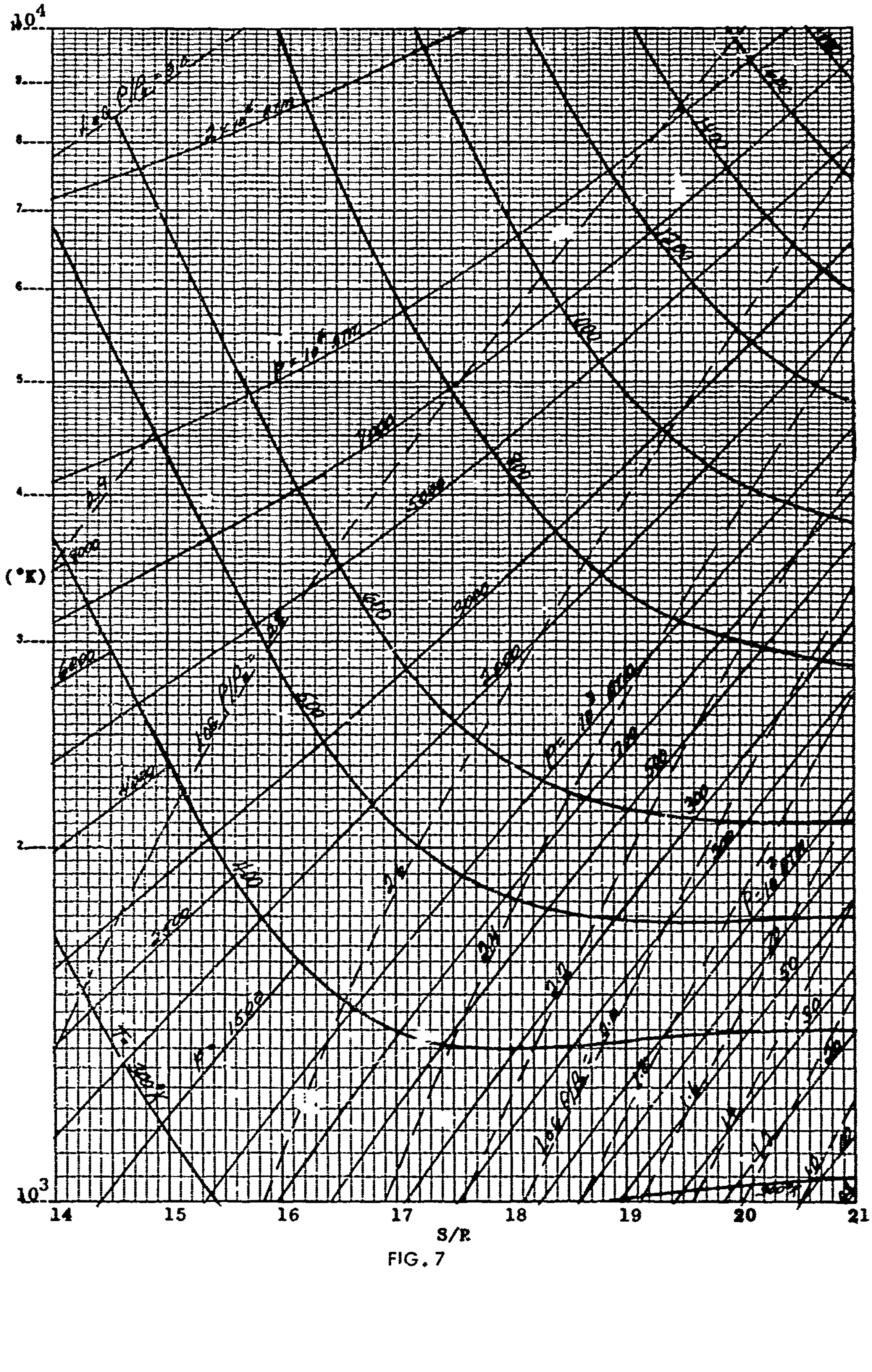


FIG. 7

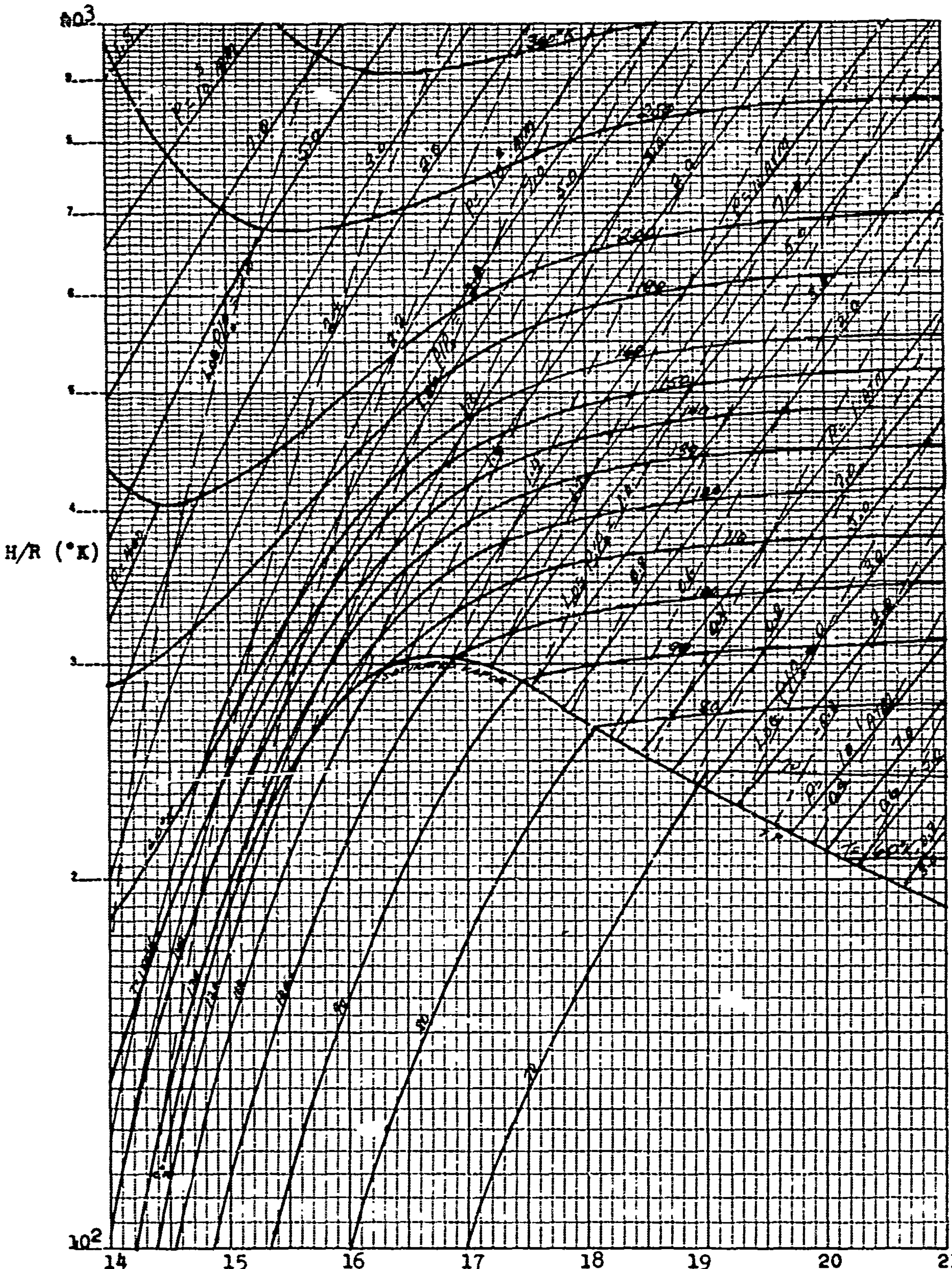


FIG. 8

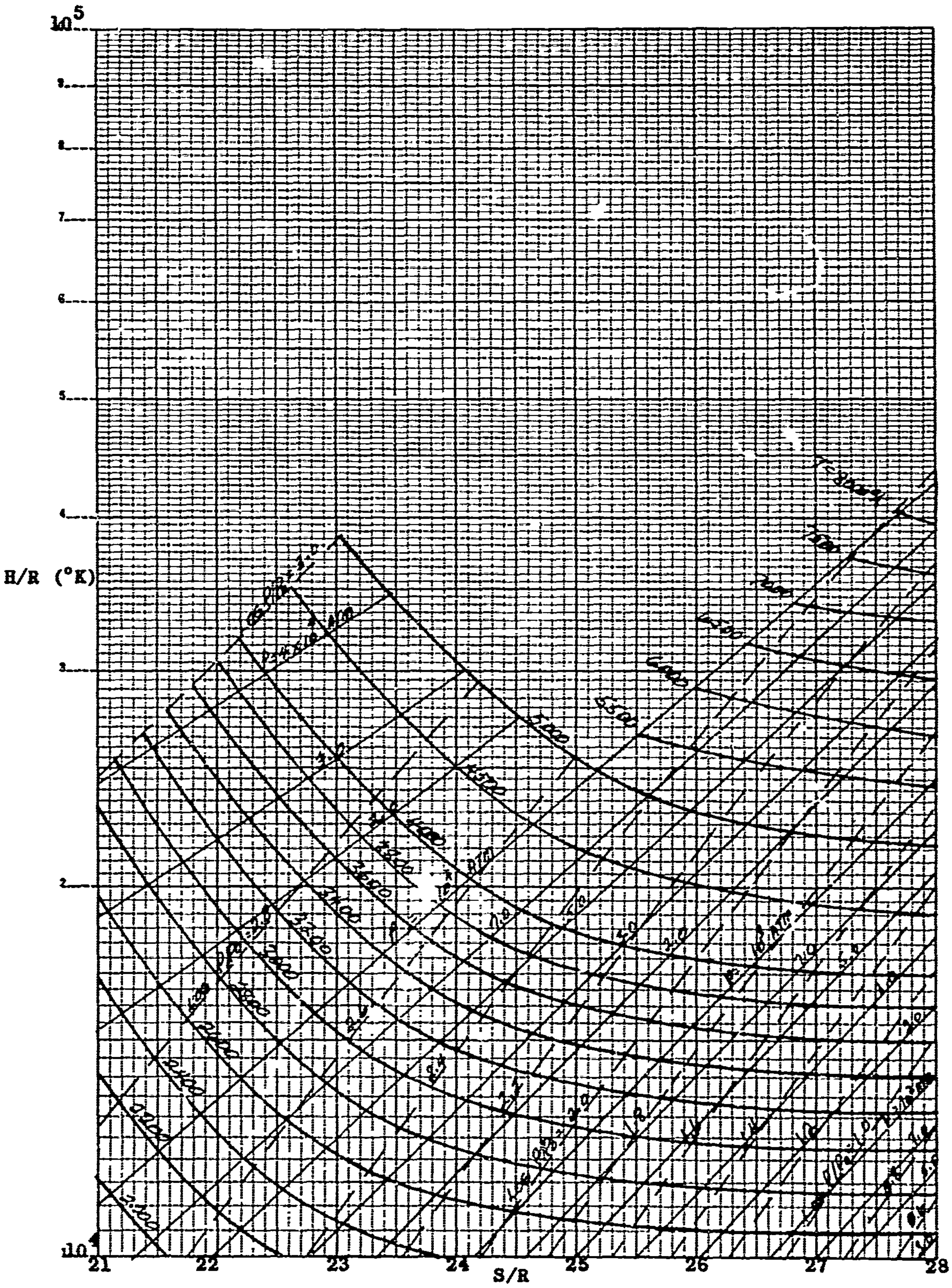


FIG. 9

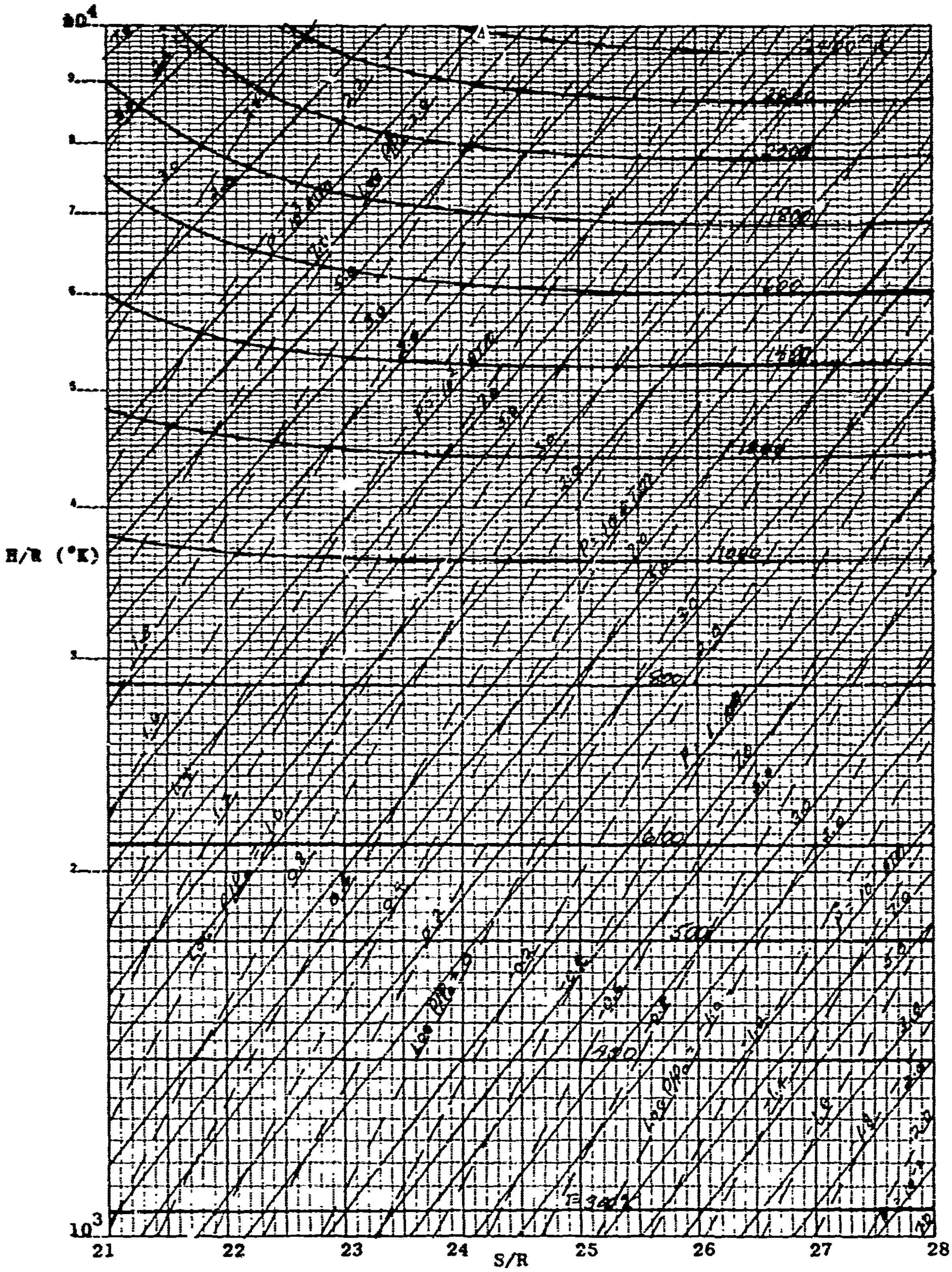


FIG. 10

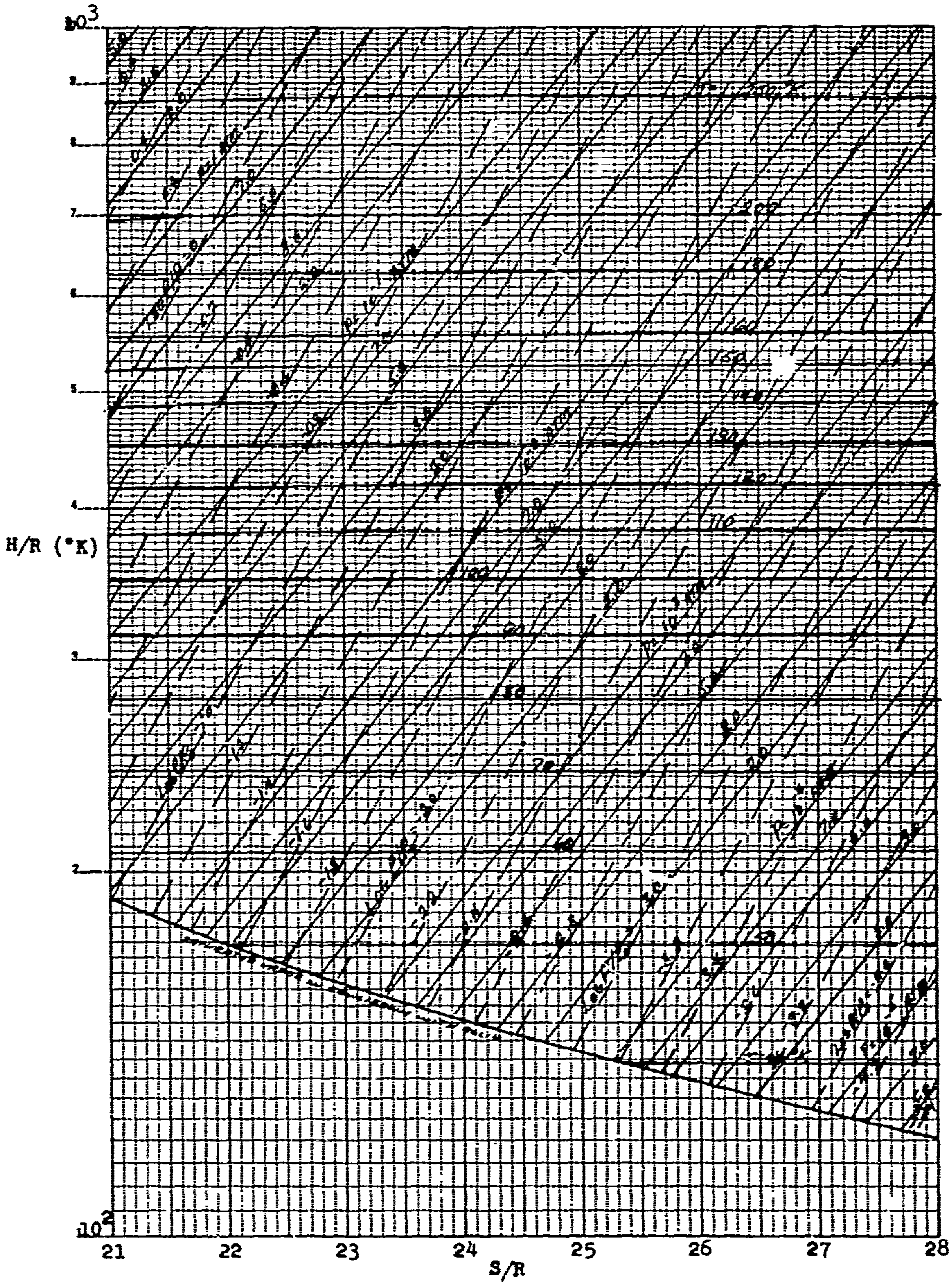
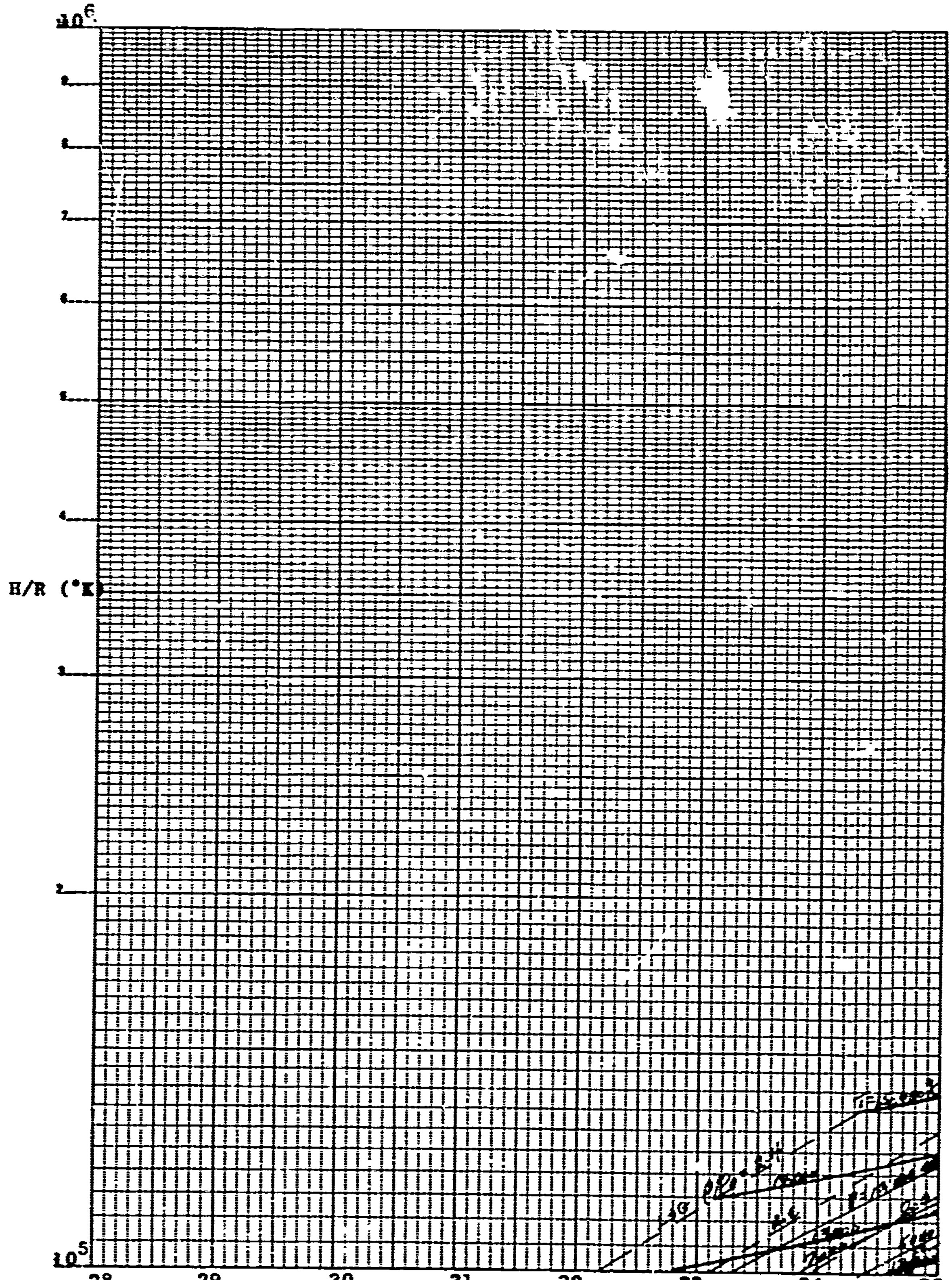


FIG. 11



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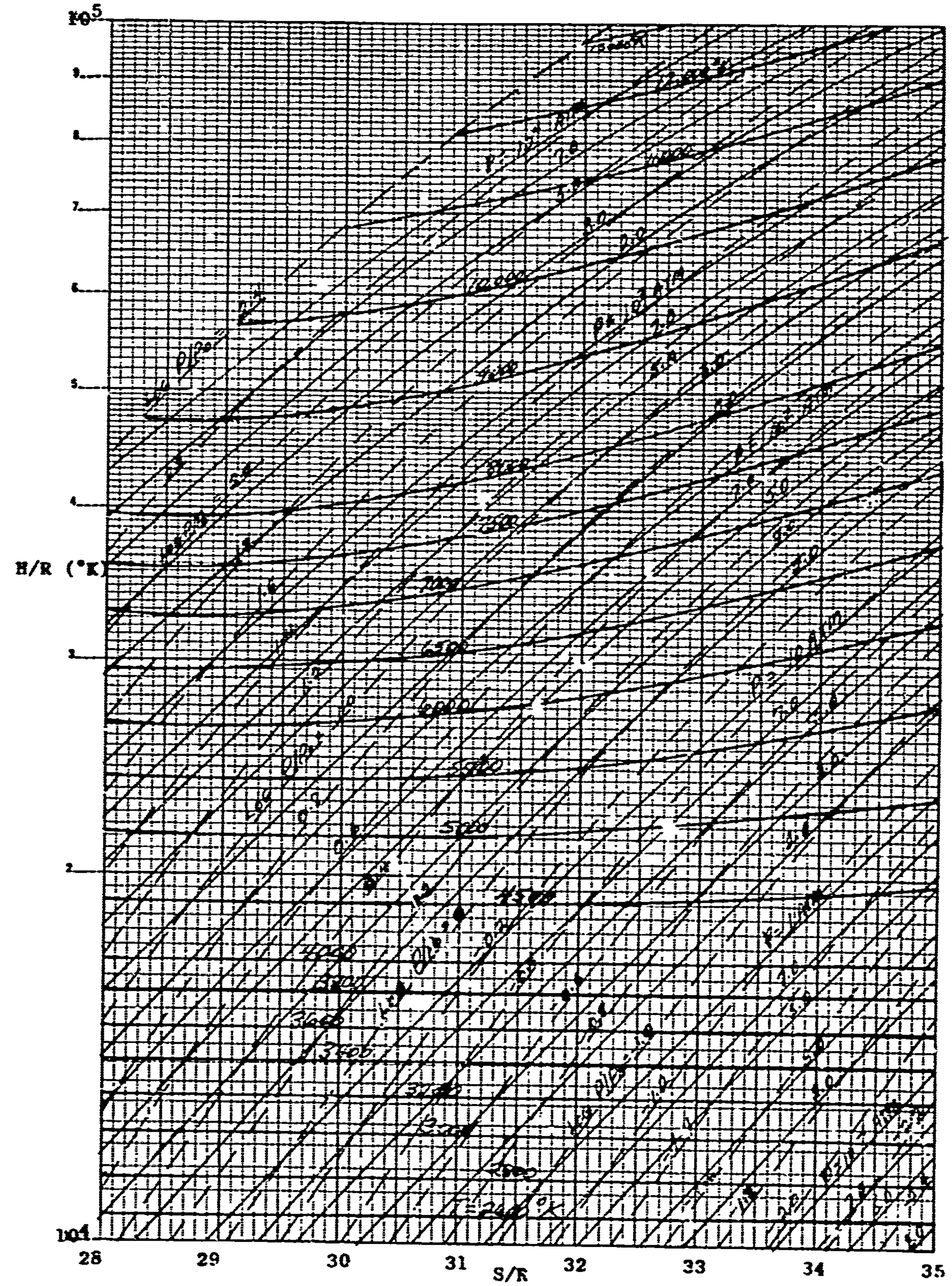
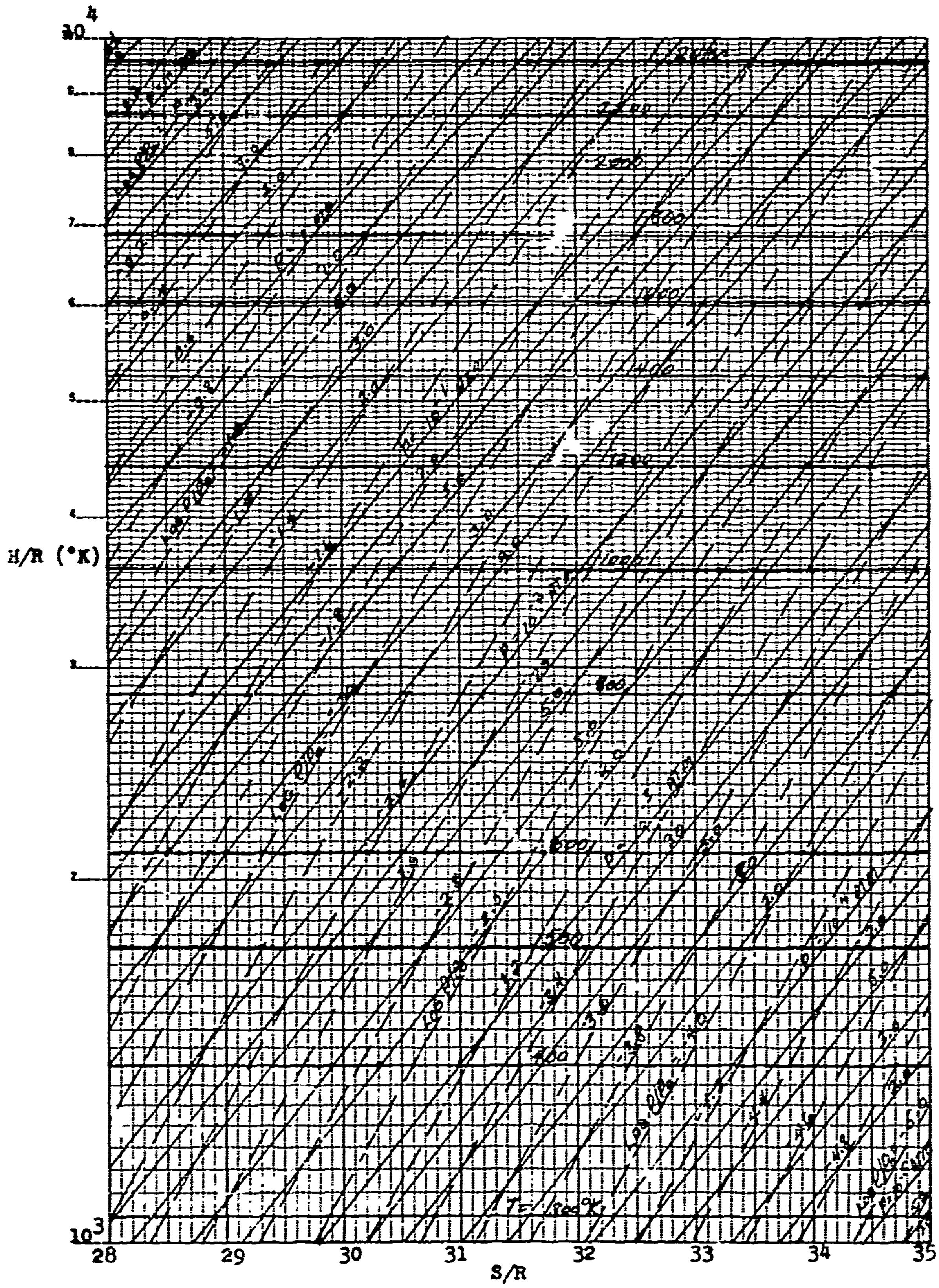


FIG. 13



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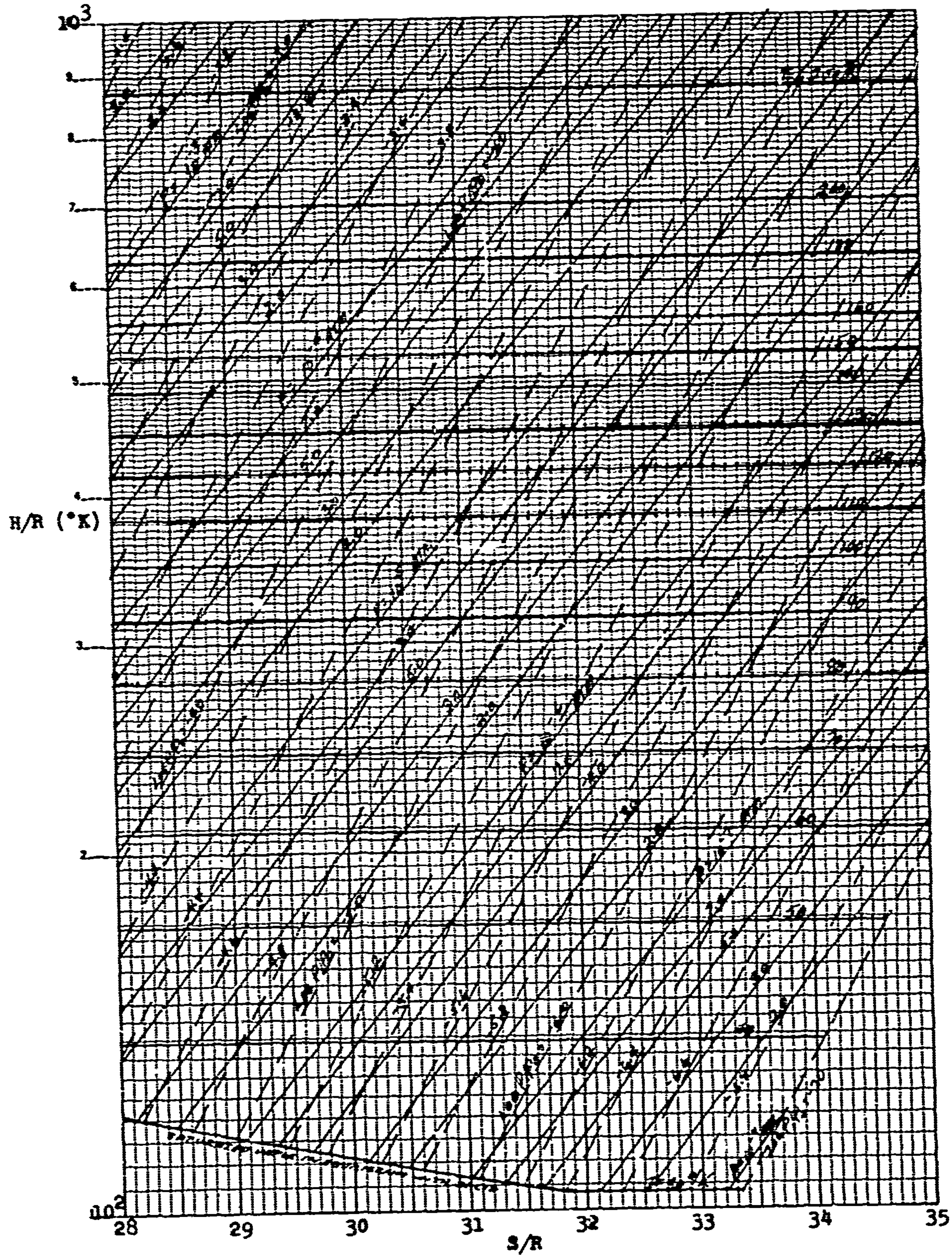


FIG. 15

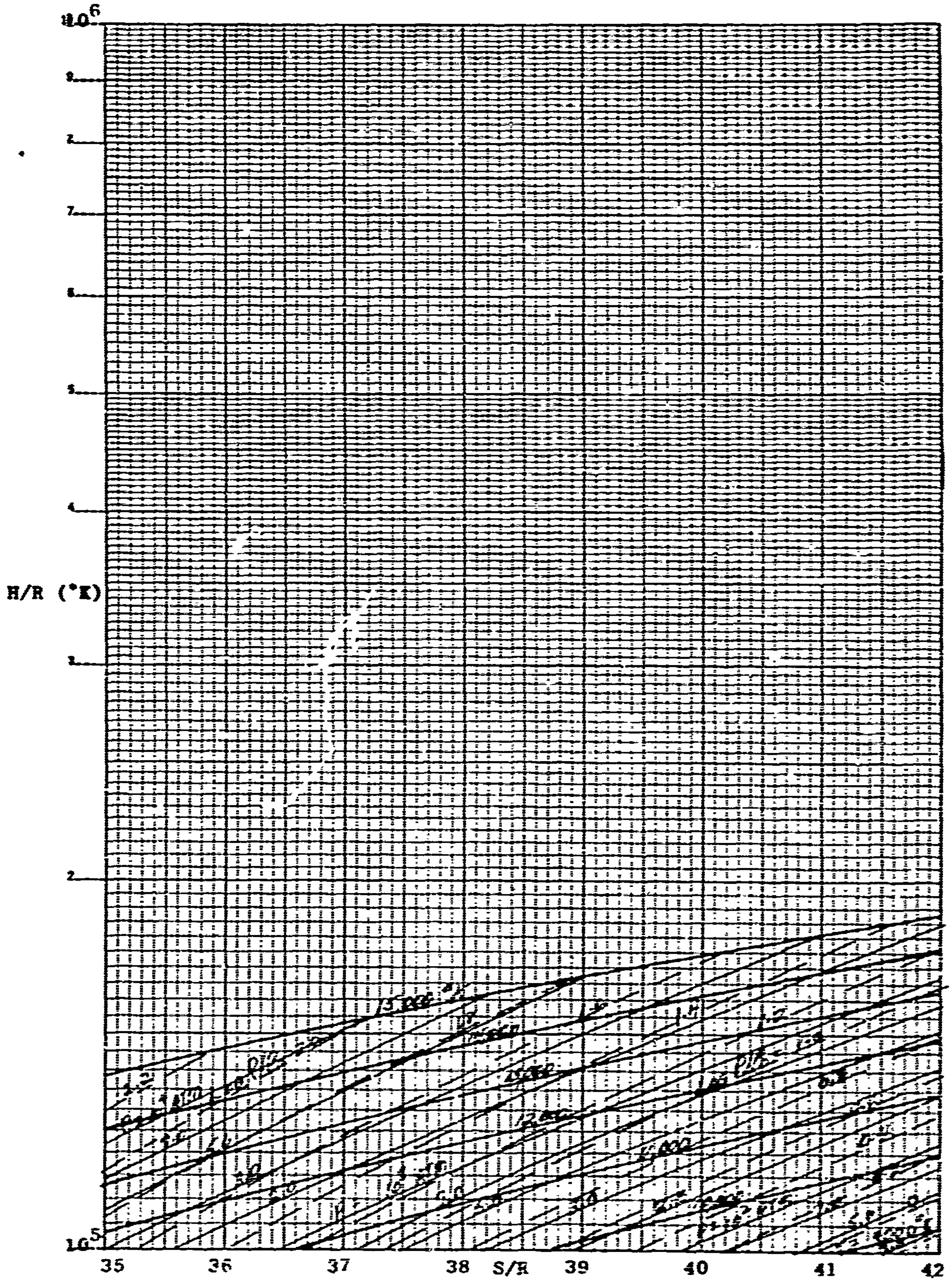


FIG. 16

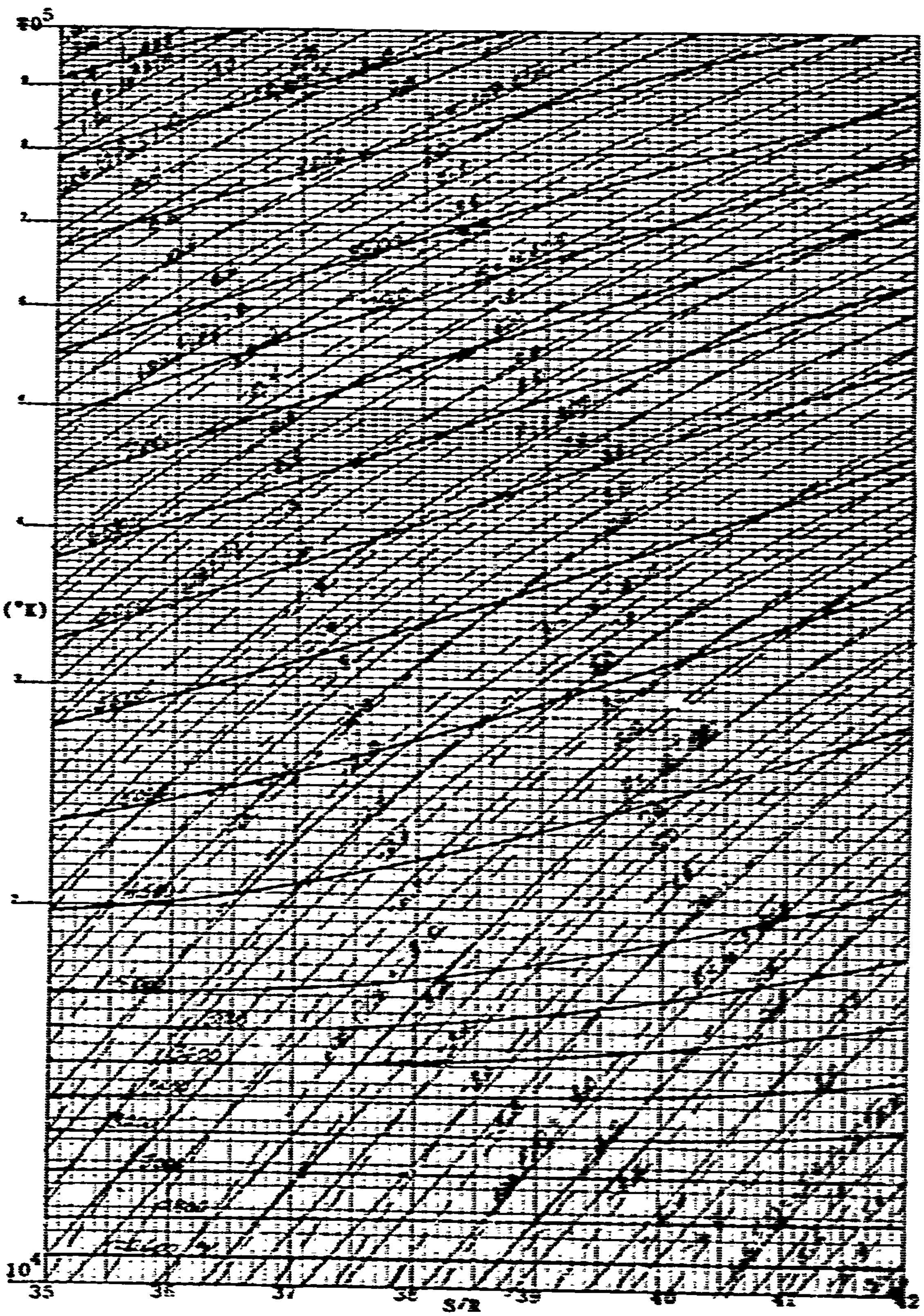
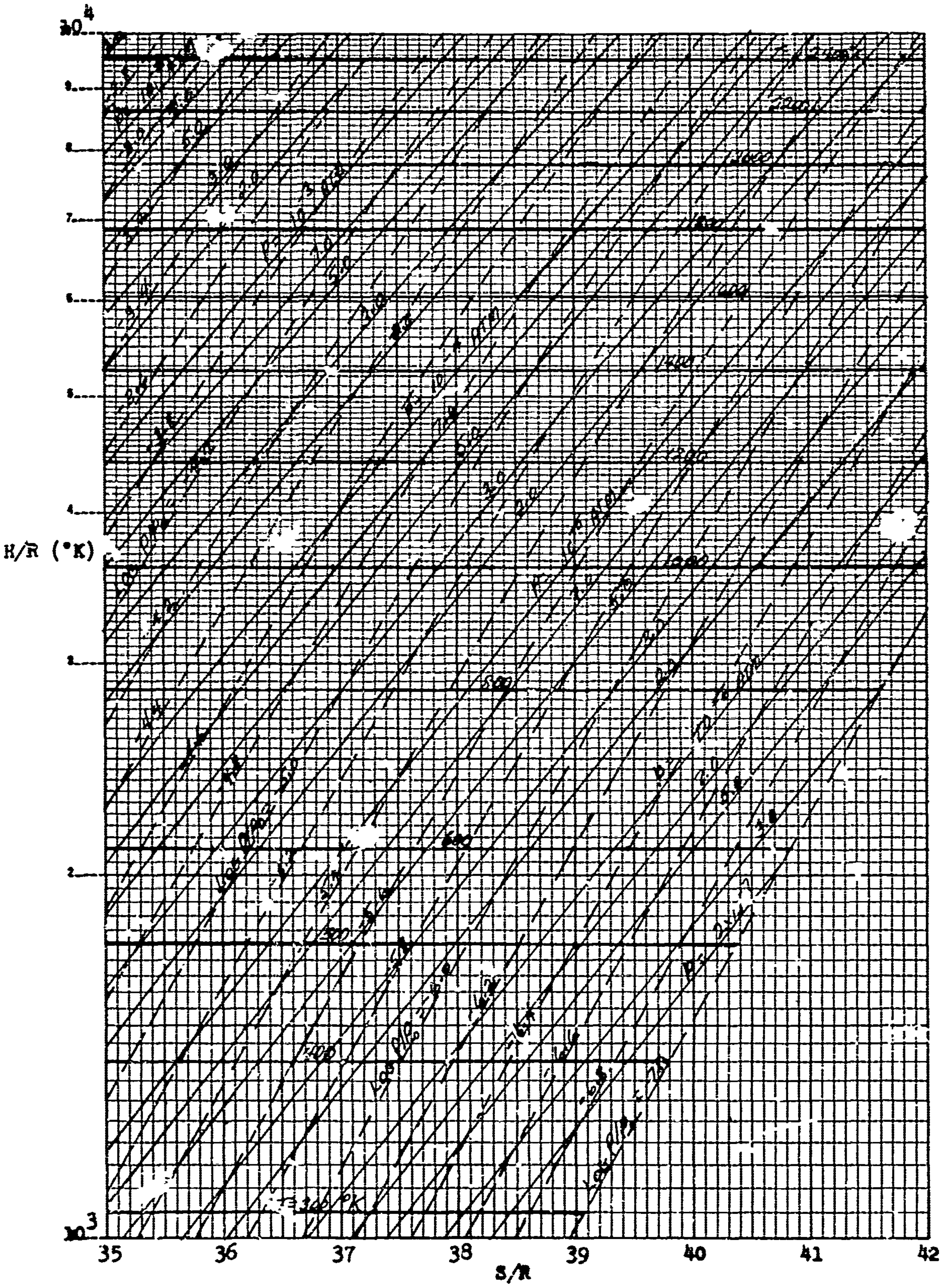


FIG. 17



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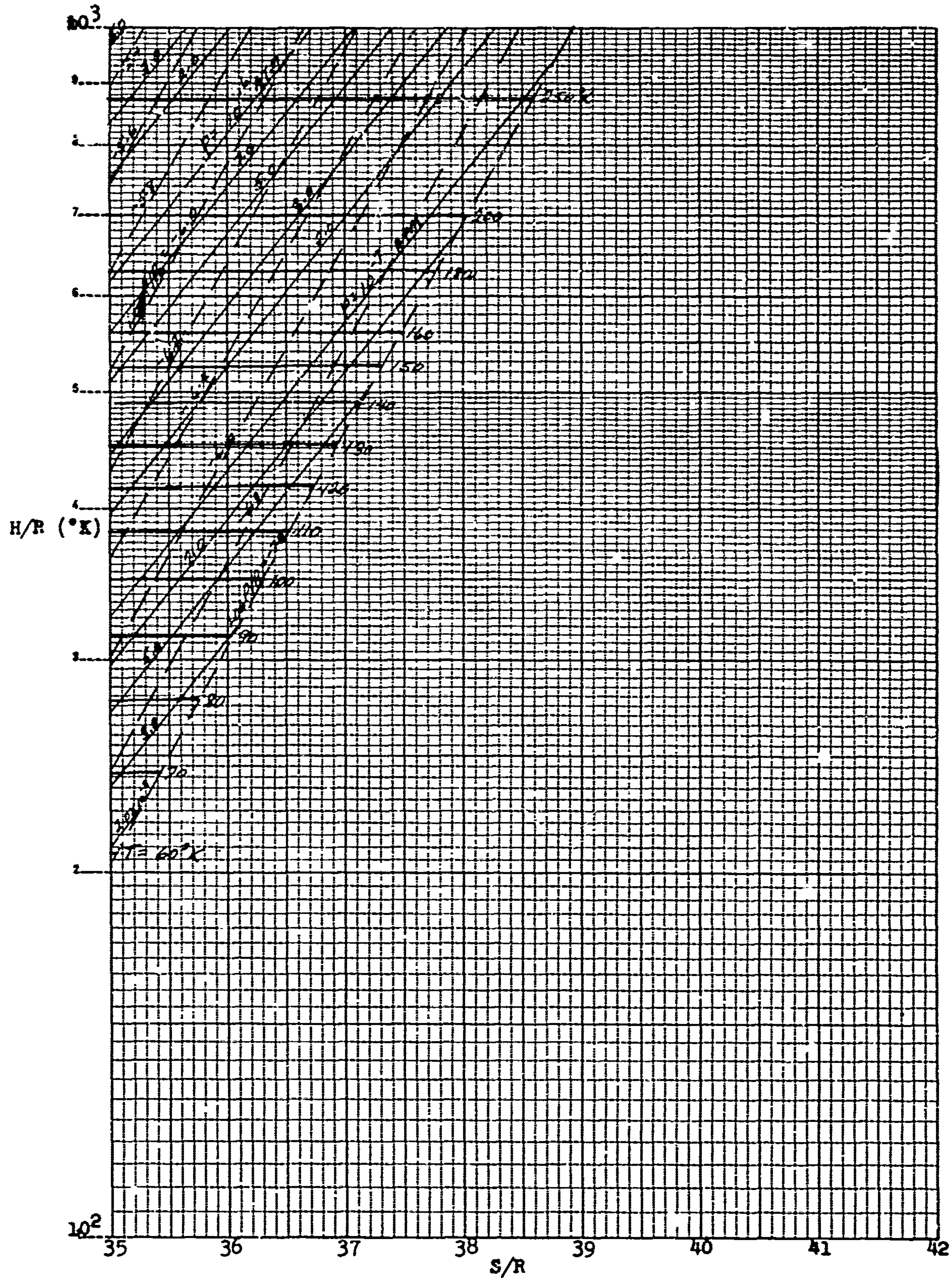

FIG. 19

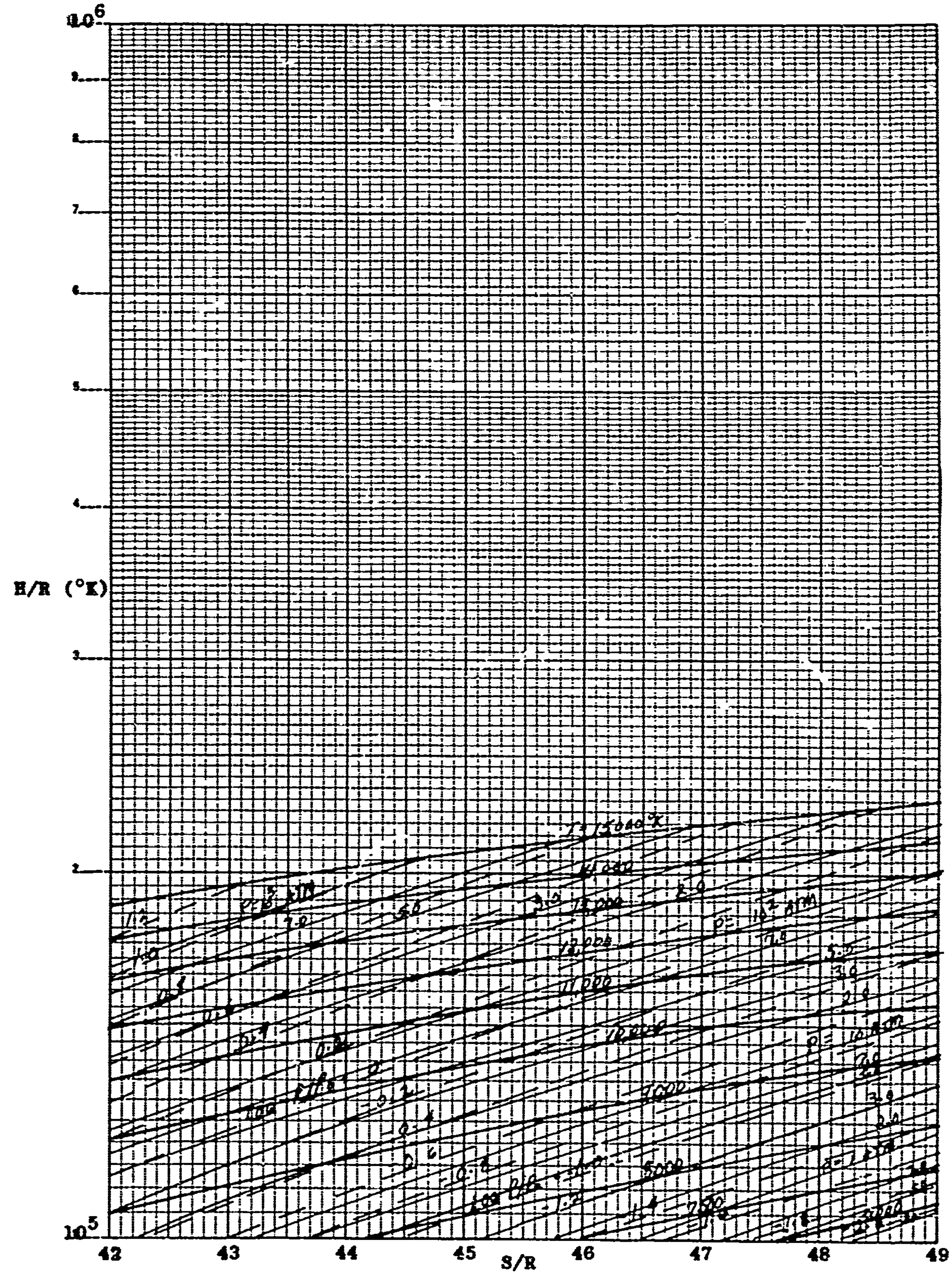

FIG. 20

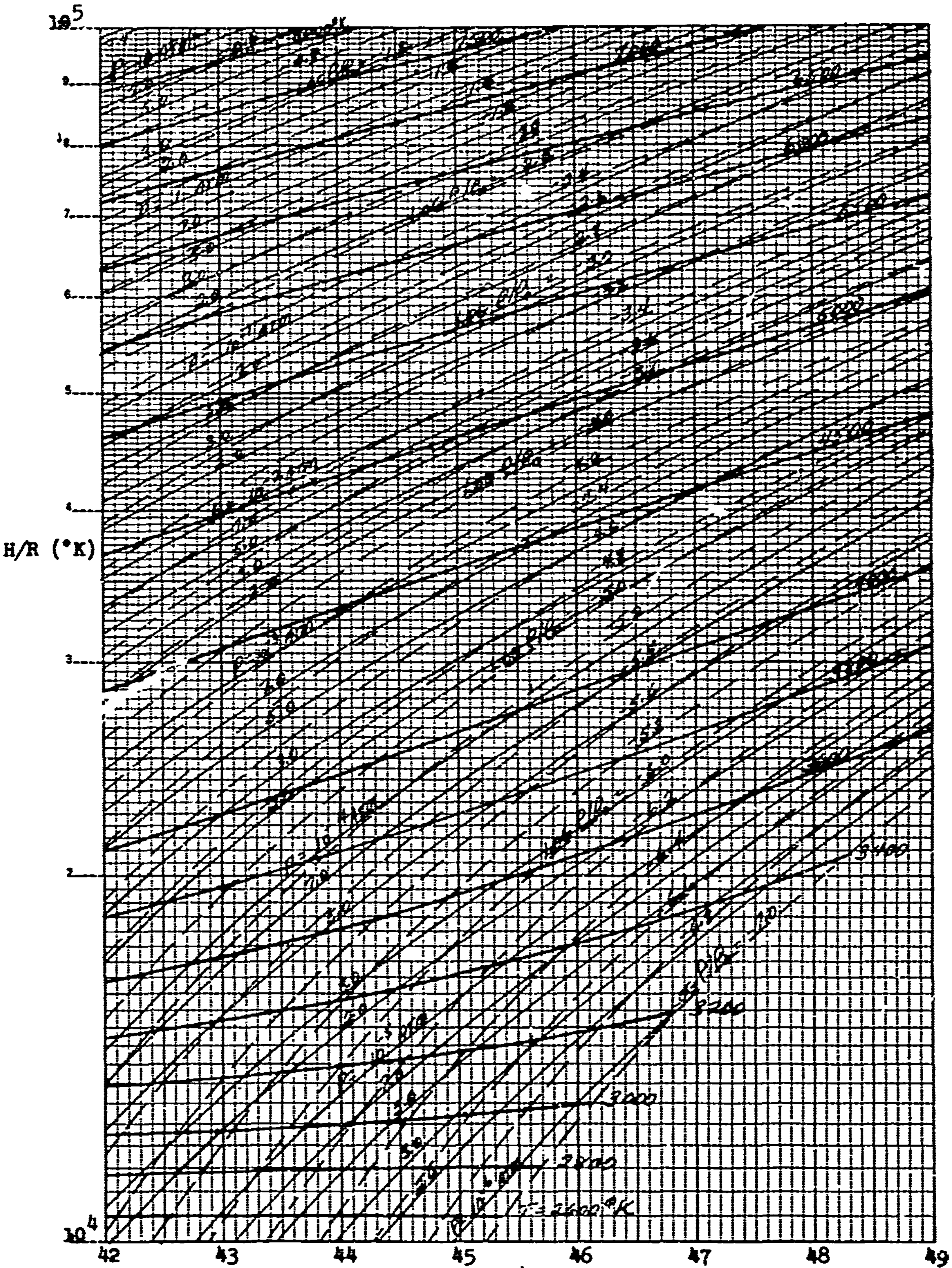
10^5
9
8
7
6
5
4
H/R (°K)
3
2
10^4
42
43
44
45
46
47
48
49
S/R
3400
3200
3000
2800

FIG. 21

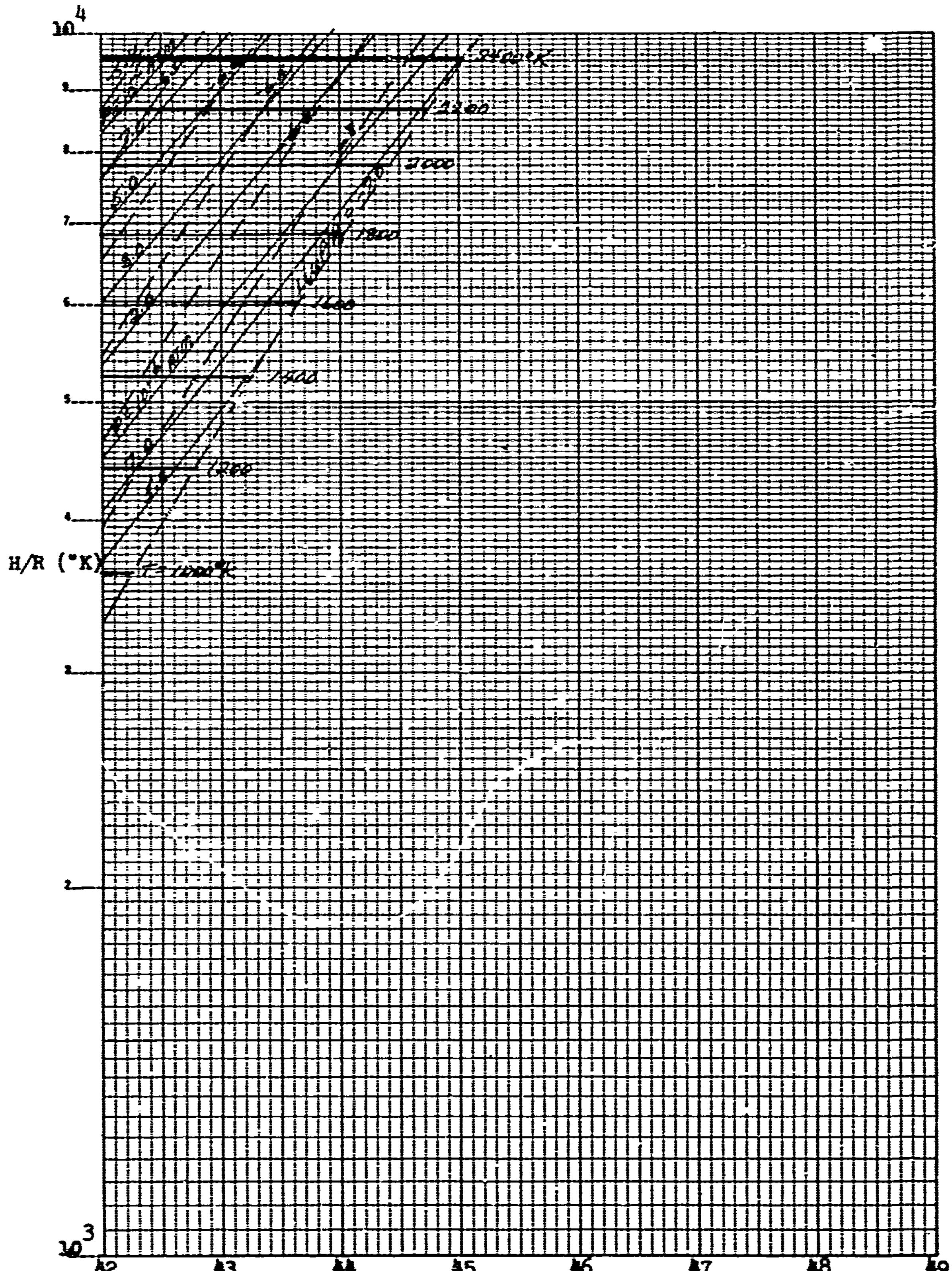

FIG. 22

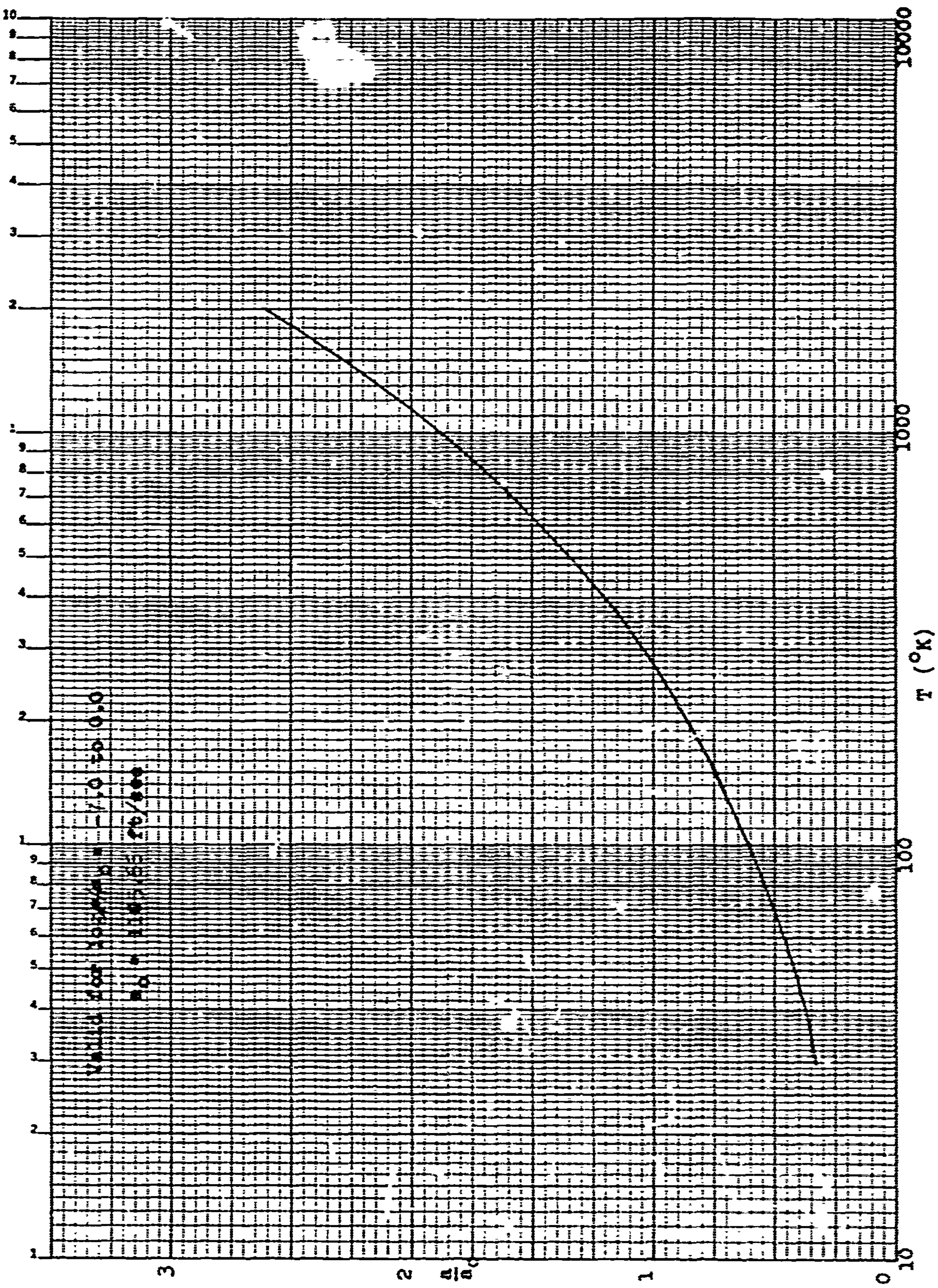

FIG. 23 ACOUSTIC VELOCITY FOR LOW TEMPERATURE NITROGEN

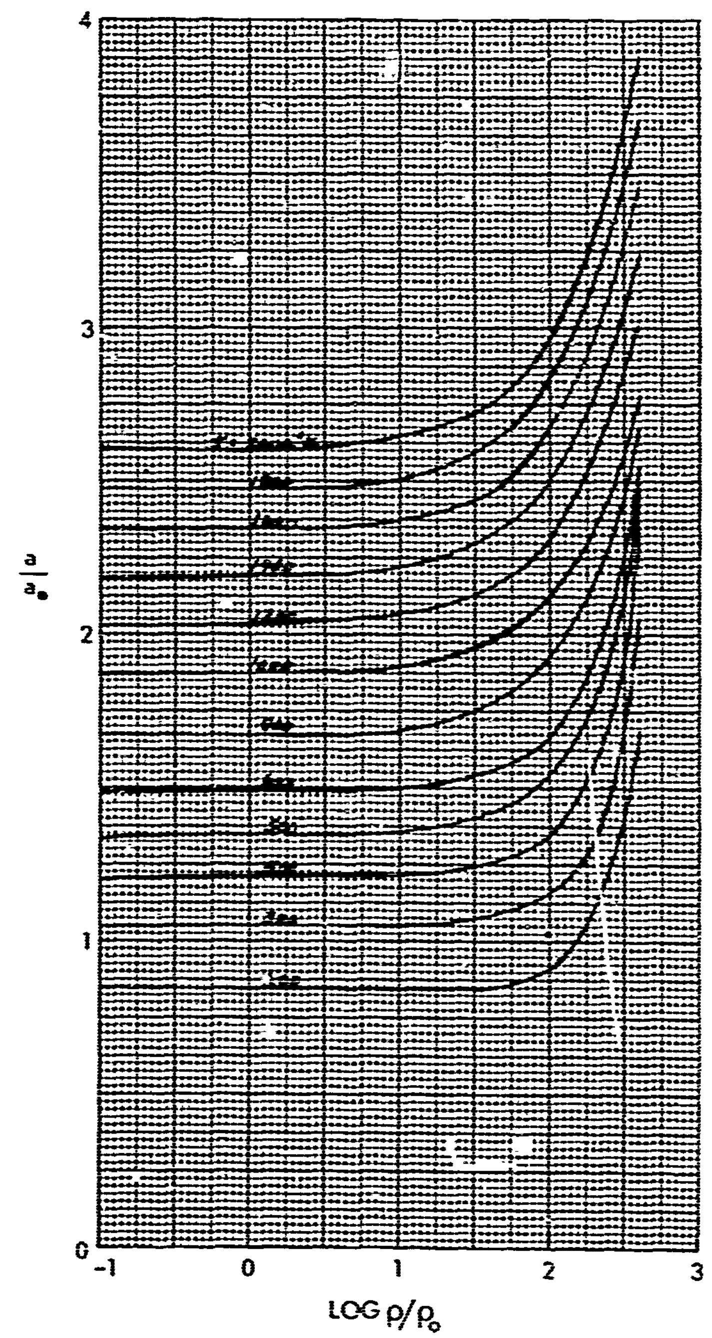

FIG. 24 ACOUSTIC VELOCITY FOR HIGH DENSITY NITROGEN

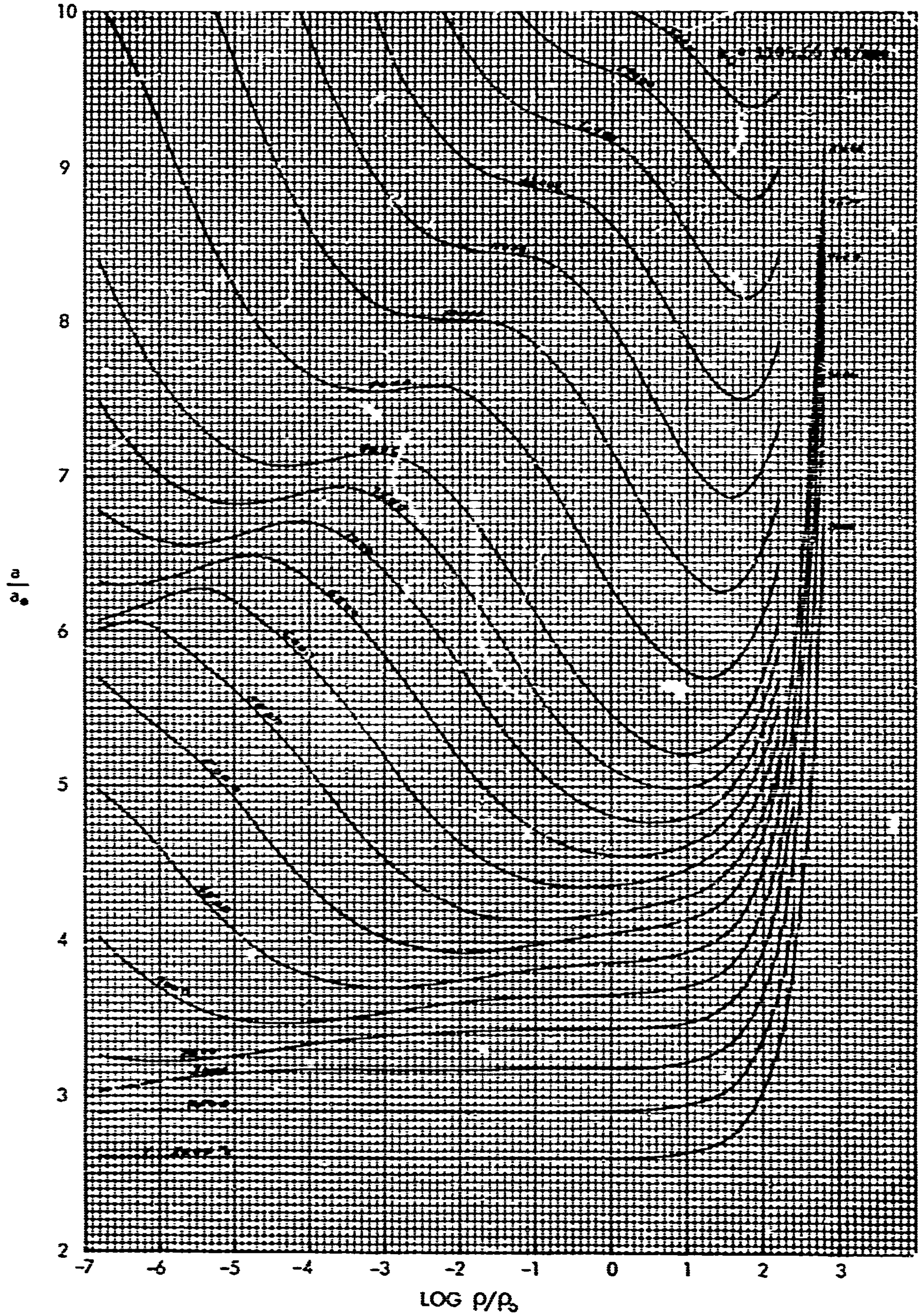

FIG. 25 ACOUSTIC VELOCITY FOR HIGH TEMPERATURE NITROGEN

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R&D

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13. ABSTRACT

Thermodynamic data for nitrogen are presented in Mollier diagram form covering the temperature range of 30°K to 15,000°K and the density range of 10^{-7} to 10^3 amagat. Data for the solid and liquid regions are included. The diagram contains all available data of interest to the worker in fluid mechanics and aerodynamics. Speed of sound data are presented on separate charts.

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gas properties						
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